



Final Technical Report: (1988-1991)

Nitration and Nitrocompounds

Contract #88-K-0361

Work Unit: 4326-832

Our work, over the years, involved new and improved methods of nitration and their application in the preparation of high energy nitrocompounds including nitramines.

(i) New nitrating systems

In the course of studying new superacid systems in nitration we evaluated the nitric-tetratriflatoboric acid system $\text{HNO}_3\text{-H}[\text{B}(\text{O}_3\text{SCF}_3)_4]$ for its nitrating ability of aromatics.

Tetratriflatoboric acid, $\text{H}[\text{B}(\text{O}_3\text{SCF}_3)_4]$ was conveniently prepared *in situ* from triflic acid (excess) and boron trichloride and could be used without any workup.

Nitration of benzene, toluene, fluorobenzene, chlorobenzene, anisole and naphthalene was studied with $\text{HNO}_3\text{-H}[\text{B}(\text{O}_3\text{SCF}_3)_4]$ in methylene chloride solution at -30°C and at room temperature. The new superacidic nitration of toluene gave very low (1%) *meta* nitration both at -30°C and at room temperature. At the same time the *ortho/para* isomer ratio is also lower than in most studied nitronium ion nitrations, indicating ion pairing or association with bulky tetratriflatoborate anion. Similarly high regio(positional) selectivity was found in nitration of the other aromatics.

Previously developed superacid systems based on triflic acid (trifluoromethanesulfonic acid) were extended to pentafluoroethanesulfonic (pentflic) acid. A number of new solid acid systems are also

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evaluated, including polymeric, solid forms of the pyridine/HF reagent, which are obtained from polyvinylpyridine and anhydrous HF.

Nitration of α,α,α -trihalomethoxybenzenes with nitronium tetrafluoroborate or methyl nitrate/boron trifluoride in nitromethane solution was studied and compared to that of halobenzenes. Predominant *para*-substitution is observed with no formation of *meta* isomer. The substrate reactivity compared to benzene (determined in competition experiments) is 0.1 to 0.3.

Table: Nitration of α,α,α -Trihalomethoxybenzenes with $\text{NO}_2^+\text{BF}_4^-$ and Comparison with Halobenzene

substrate (ArH)	reagent	solvent	temp. °C	k _{ArH} / l/g	Stoichiometric distribution		
					ortho	meta	para
o-Chloro-o,a-difluoro- methoxybenzene	$\text{NO}_2^+\text{BF}_4^-$	CH_3NO_2	25	0.3	-	-	>99
	$\text{CH}_3\text{ONO}_2\text{-BF}_3$	CH_3NO_2	25	0.1	-	-	>99
o,a-Dichloro-a-fluoro- methoxybenzene	$\text{NO}_2^+\text{BF}_4^-$	CH_3NO_2	25	0.3	trace	-	>99
	$\text{CH}_3\text{ONO}_2\text{-BF}_3$	CH_3NO_2	25	0.3	trace	-	>99
o,a,a-Trifluoro- methoxybenzene	$\text{NO}_2^+\text{BF}_4^-$	CH_3NO_2	25	0.2	-	-	89
	$\text{CH}_3\text{ONO}_2\text{-BF}_3$	CH_3NO_2	25	0.1	10	-	70
o,a,a-Trichloro- methoxybenzene	NO_2BF_4	CH_3NO_2	25	0.2	11	-	89
	$\text{CH}_3\text{ONO}_2\text{-BF}_3$	CH_3NO_2	25	0.2	10	-	90
Fluorobenzene	$\text{NO}_2^+\text{BF}_4^-$	sulfolane	25	0.5	9	0	91
	$\text{CH}_3\text{ONO}_2\text{-BF}_3$	CH_3NO_2	25	0.1	11	4	85
Chlorobenzene	$\text{NO}_2^+\text{BF}_4^-$	sulfolane	25	0.1	23	0.7	77
	$\text{CH}_3\text{ONO}_2\text{-BF}_3$	CH_3NO_2	25	0.1	23	trace	77
Bromobenzene	$\text{NO}_2^+\text{BF}_4^-$	sulfolane	25	0.1	26	1	73
	$\text{CH}_3\text{ONO}_2\text{-BF}_3$	nitromethane	25	0.1	25	1	74

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Studying new applications of the nitronium tetrafluoroborate nitrating system we have now found that when reacting sterically crowded 2,6-di and 2,4,6-tri-*tert*-butylpyridine with nitronium tetrafluoroborate nitration occurred exclusively in the ring. Thus, when 2,6-di-*tert*-butylpyridine was reacted with $\text{NO}_2^+\text{BF}_4^-$ in dry CH_2Cl_2 or CH_2Cl_2 /sulfolane, apart from unreacted starting material, 28% 2,6-di-*tert*-butylpyridine and 6% 2,6-di-*tert*-butyl-3,4-di-nitropyridine were formed.

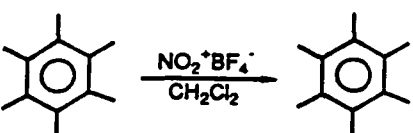
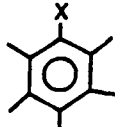
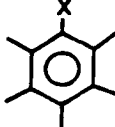
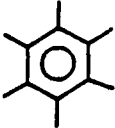
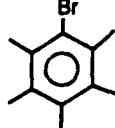
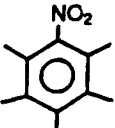
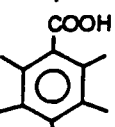
Similarly, 2,4,6-tri-*tert*-butylpyridine when reacted with $\text{NO}_2^+\text{BF}_4^-$ in CH_2Cl_2 gave 36% 2,4,6-tri-*tert*-butyl-3-nitropyridine.

In continuation of our study of superacid catalyzed nitration systems we extended previous solution studies to solid superacid catalyzed gas phase nitration of toluene with N_2O_4 at 190°C . The reaction was studied both in a static pressure system and in an atmospheric flow system. The observed drastic change to predominant *ortho-para* nitration in the acid catalyzed reactions, compared to the non-catalyzed typical radical nitration, clearly shows the high efficiency of the solid superacids for effecting electrophilic nitration.

Gas Phase Nitration of Toluene with N_2O_4 at 190°C

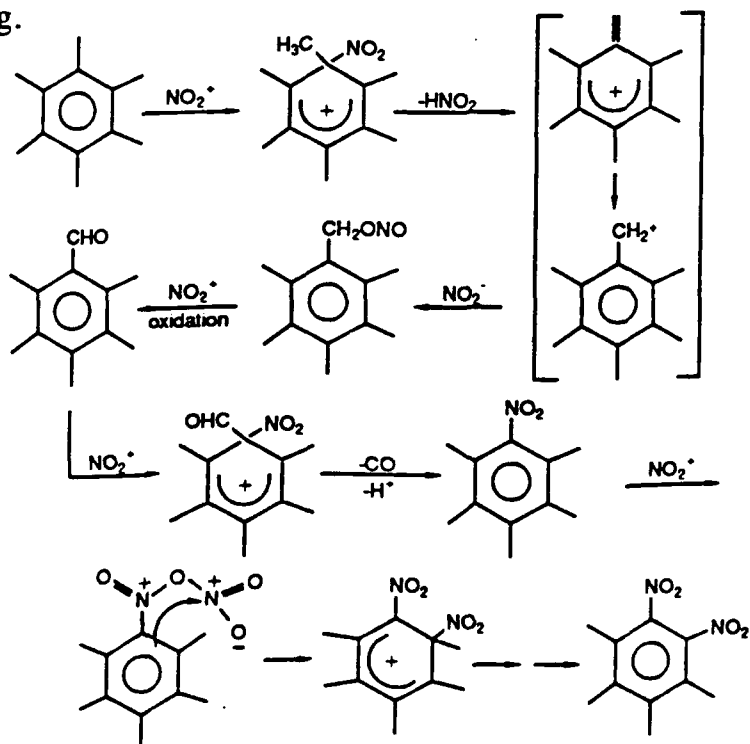
<u>Static pressure reaction</u>	% Isomer Distribution		
	<u>ortho</u>	<u>meta</u>	<u>para</u>
no catalyst	21	54	25
Nafion-H	48	7	45
<u>Flow system</u>			
Nafion-H	71	10	19
TaF ₅ /Al ₂ O ₃	76	6	18

Exploring the nitronium tetrafluoroborate nitration method of aromatics an unexpected new reaction was found in converting hexamethylbenzene (or its monosubstituted analogs) to dinitroprehnitenes in nearly quantitative yield. Synthesis of such *ortho*-dinitro derivatives otherwise is extremely difficult.

		
	 : $\text{NO}_2^+\text{BF}_4^-$	Yield ^a of Dinitroprehnitene
	1 : 6.5	95%
	1 : 5	90%
	1 : 4	96%
	1 : 5	92%

a) isolated yield, product characterized by spectroscopic means.

The mechanism of the observed new nitration reaction can be suggested as the following.

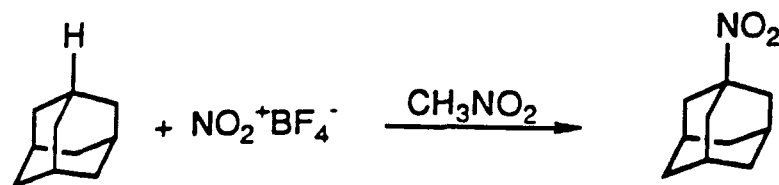


Practical applications were further explored using solid perfluoroalkanesulfonic acids, such as perfluorodecanesulfonic acid and Nafion-H in conjunction with boron trifluoride. For the efficient preparation of TNT low *meta* nitration is of significance.

Studies were initiated using nitric acid-trifluoromethanesulfonic anhydride as nitrating agent.

(ii) Electrophilic nitration of σ -bonds

Nitration of adamantane with nitronium tetrafluoroborate in highly purified, dry, nitrile-free nitromethane gave 1-nitroadamantane in 66% isolated yield. Similar nitration of diamantane gave 1-nitrodiamantane in 62% yield with 5% of 4-nitrodiamantane. In commercial nitromethane which contains upto 5% propionitrile, N-adamantylpropionamide is the major reaction product due to predominant Ritter reaction. Commercial nitroethane is free of nitriles and in it nitration of adamantane gave 1-nitroadamantane in 74% isolated yield. In studying the mechanism, competitive nitration of equimolar amounts of adamantane and 1,3,5,7-tetradeuterioadamantane gave a kinetic hydrogen isotope effect of $k_H/k_D = 1.31 \pm 0.06$. The isotope effect determined intramolecularly by nitrating 1-deuterioadamantane was found to be $k_H/k_D = 1.2 \pm 0.11$. The small isotope effect is interpreted as the consequence of a highly unsymmetrical five coordinate carbocationic transition state, although a two step mechanism with a carbocationic intermediate and no primary isotope effect, with proton elimination step being not rate determining, can not be *per se* eliminated. Initial SET to the nitronium ion and subsequent radical nitration by $\text{NO}_2\cdot$ is less probable.



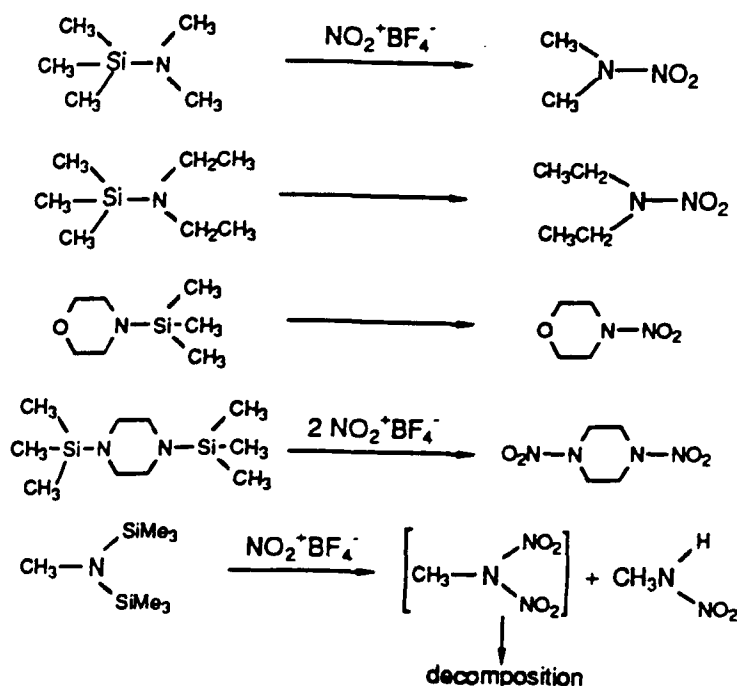
We also attempted nitration of dodecahedrane with nitronium tetrafluoroborate (in cooperation with Prof. Leo Paquette of Ohio State University), but the results were inconclusive.

(iii) ^{15}N NMR Spectroscopic investigation of nitrous and nitric acids in sulfuric acid solutions.

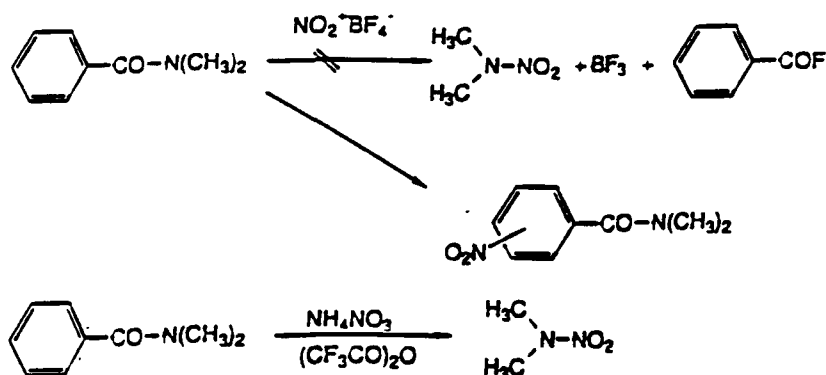
Both nitrous and nitric acids were studied in sulfuric acid solutions of varying acid strengths by ^{15}N NMR spectroscopy. The study gives new insights into the nature of intermediates present at different acid strengths. Furthermore, we have also discovered a novel redox reaction between NO_2^+ and NO^+ ions involving the intermediacy of their respective acids. A mechanism was also proposed to explain the observed exchange involving the corresponding nitric and nitrous acids.

(iv) Preparation of nitramides (acid-free nitration)

The continued study of the new preparation of nitramides via $\text{NO}_2^+\text{BF}_4^-$ nitration of the corresponding trimethylsilylamides was investigated. Some of the effective, high yield nitrations were the following.



We also carried out studies of the nitration of N,N-dialkylbenzamides to nitramides. $\text{NO}_2^+\text{BF}_4^-$ is not suited for these nitration, as the reaction results in nitration of the aromatic ring. $\text{NH}_4\text{NO}_3/(\text{CF}_3\text{CO})_2\text{O}$, however, was found to be highly effective to carry out the reaction.



(v) Nitration of phenylboron dichloride with $\text{NO}_2^+\text{BF}_4^-$

To probe the nitration of boron substituted hydrocarbons we have studied the nitronium tetrafluoroborate nitration of phenylboron dichloride.

Electrophilic nitration of phenylboron dichloride with nitronium tetrafluoroborate and N-nitro-2,4,6-collidinium tetrafluoroborate was investigated in nitromethane solution. The reaction give 10-18% *ortho*, 67-69% *meta*, and 15-21% *para* isomer. NMR studies of the systems also show the formation of PhBFCl and PhBF_2 by fluoride exchange as well as their intermediate complexes with the BF_4^- anion. The high *meta* content is attributed to the nitration of uncomplexed phenylboron dihalides with the $-\text{BX}_2$ group exhibiting $-I$ effect which directs the nitration significantly to the *meta* position. High *para* isomer content was obtained when the phenylboron dihalides were mostly complexed by the BF_4^- anion thereby reducing the $-I$ effect of $-\text{BX}_2$ group.

The nitration of iodosobenzene dichloride gave essentially only nitroiodobenzenes due to the dissociation of PhICl_2 and the much faster nitration of PhI as compared to PhICl_2 .

Attempted nitration of PhICl_2 with $\text{NO}_2^+\text{BF}_4^-$ in CH_3NO_2 led only to oxidation. The oxidation could not be prevented even when using trimethylphosphate as solvent or the milder nitrating agent, $\text{MeONO}_2/\text{BF}_3$.

(vi) Study of the role of protosolvation in activating the nitronium ion

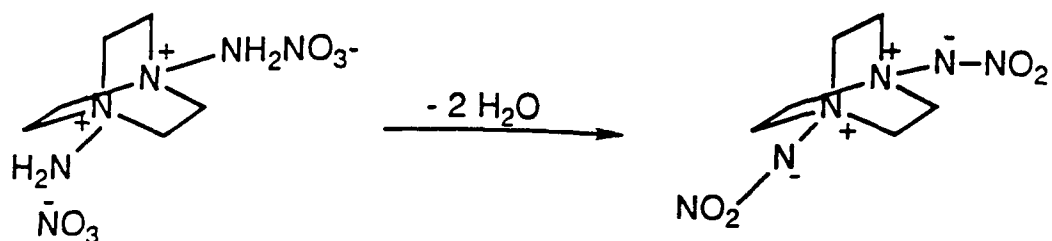
The linear nitronium ion as isolated salt, such as the tetrafluoroborate, is generally used in aprotic solvents (sulfolane, nitromethane, acetonitrile) for the nitration of aromatics and various other substrates. It was found in our preceding work that in nitrating saturated hydrocarbons, the reactivity of the nitronium ion is greatly enhanced when carrying out the reactions in the presence of strong acids.

Work was now extended to the study of the nitration of deactivated aromatics, specifically di- and trifluoronitrobenzenes. Triflic acid is a very suitable acid for these reactions and dinitro di- and trifluorobenzenes were obtained in good yield. In much stronger Magic Acid® ($\text{FSO}_3\text{H}:\text{SbF}_5$) solution the yields improved further. In these highly acidic systems in all probability, the reactivity of the nitronium ion is further enhanced by protosolvation.

(vii) Preparation of hydrazinium nitrates and energetic amine nitroamides

A convenient one-step preparation of hydrazinium nitrates by the reaction of tertiary amines or azaarenes with hydroxylamine-O-sulfonic acid and barium nitrate in the presence of barium oxide was developed. (This work was originally supported by ONR on New Energetic Material project, but the support was discontinued.) Hydrazinium nitrates are easily transformed to amine-nitroimides with trifluoroacetic acid chloride

in trifluoroacetic acid using Katritzky's procedure even in case of bridgehead nitrogen systems. Remarkably stable highly energetic compounds such as Dabco-1,4-bis-nitroimide were obtained in good preparative yield. Spectroscopic and x-ray structural studies for the prepared compounds substantiate the proposed structures.



Publications Supported by ONR (1988-1991)

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Prakash, G. K. S., Wang, Q., Li, X-Y., Olah, G. A. Highly Regioselective Nitration of Hexamethylbenzene and Its Derivatives to Dinitroprehnitene with Excess Nitronium Tetrafluoroborate, *Helv.Chim.Acta*, **73**, 1167 (1990).

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